Anticorrosive performance of MoO_4^{-2}-doped polyaniline conductive polymer

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Abstract

Electrodeposition polyaniline (PANI) and polyaniline doped (PANI-MoO_4^{-2}) coatings on steel was prepared in oxalic acid solution by potentiodynamic polarization technique. Morphology of the surface coatings was analyzed by scanning electron microscopy (SEM). The protective properties and electrochemical behavior of such coatings in $0.5M H_2SO_4$ pH0.3 solution were investigated using open-circuit potential versus time of exposure and electrochemical impedance spectroscopy (EIS). It was shown that PANI coating presented an anodic protection and their doping by molybdate ions increased considerably the protection time.

Keywords: Anodic protection, Corrosion, Polyaniline, Sodium molybdate, Steel.

I. Introduction

The protection of mild steels against corrosion by a layer of conductive polymer CP has gained significant attention in recent years. Conductive polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) have been studied for their potential in providing corrosion protection to mild steel [1-5]. Research literature has demonstrated a noticeable enhancement of protection of ferrous materials against corrosion using conducting polymers as coatings, making them an ideal potential for corrosion protection of mild steel and other ferrous alloys. These CP produce a galvanic effect characterized as anodic protection, where the oxidizing power of the CP is capable of setting the metal in a passive state. This has been particularly observed in the case of iron and ferrous metals [3, 6].

The electropolymerization of aniline has been the subject of numerous studies since its first use in 1985, when DeBerry showed that the PANI deposited electrochemically reduced significant the rate of corrosion of steel in acidic environment [7]. These coatings can be applied individually or as a primer layer in a coating system [8]. Research has shown that the addition of dopants can influence the corrosion protection behavior of polyaniline coatings on metals such as mild steel [9] and 304 stainless steel [10]. The influence of molybdate ion dopants in corrosion protection behavior of polyaniline coating on mild steel has been investigated, and it was found that the dopants can affect the long-time corrosion resistance of the coated metal [11].

Different protection mechanisms of polyaniline (PANI) coatings have been proposed, including anodic protection, barrier protection, corrosion inhibition, and the shift of the electrochemical interface. Studies have shown evidence of the anodic protection of PANI coatings, as indicated by the shift in the corrosion potential to the passive region and an increase in the polarization resistance for the metal [10].

In this work, a description of the synthesis conditions of doped PANI-MoO_4^{-2} and non-doped PANI coatings and corrosion tests in H_2SO_4 pH0.3 will be reported.

II. Material and methods

PANI (ANI from PanReac AppliChem, purity 99 %) coatings were deposited on the pretreated steel surface at the potential 300 V/SSE in oxalic acid solution ($C_2H_2O_4$) containing 0.1 M of aniline. The various concentrations of ions (MoO_4^{-2}) are added to the synthesis medium in the form of sodium molybdate Na_2MoO_4 (from Fluka, purity 99 %). Oxygen bubbles evolved at the beginning of the process during synthesis and by consequent, a rotating disk electrodes was necessary for remove it.

All electrochemical experiments were carried out at room temperature ($\theta = 25 \pm 0.1°C$) with a three electrode cell arrangement; a counter electrode made of a large platinum

grid, a working electrode (steel, Φ = 10 mm) and a sulfate reference electrode in saturated K_2SO_4 solution (SSE).

Before each measurement, the exposed area of the working electrode was polished and washed with double deionized water to ensure the same initial surface state.

Corrosive tests were carried out in 0.5M H_2SO_4 solutions with OCP versus time of exposure and electrochemical impedance spectroscopy (EIS).

The morphology and the elemental composition of the PANI and PANI-MoO_4^{-2} coatings was examined with FEI Quanta 200 Scanning electron microscope (SEM) coupled with an Isis X-Ray analysis system energy dispersive X-rays (EDX).

III.   Results and discussion

A.   Influence of electrolyte concentration

As we know, the electrodeposition of polymers on steel surface directly is difficult, the formation of a passive layer is required [12, 13]. Based on the search results and after preliminary experiments [8, 14], a potentiostatic electropolymerization at 300 mV/ SSE was chosen.

We have tested several electrolyt at different concentrations (oxalic acide, phosphoric acide, sulfuric acide) and the best result after the corrosion test is obtained in oxalic acid medium at different concentrations as shown in figure 1. After synthesis, PANI coatings are rinsed with distilled water, dried and then immersed in H_2SO_4 0.5M (pH 0.3).
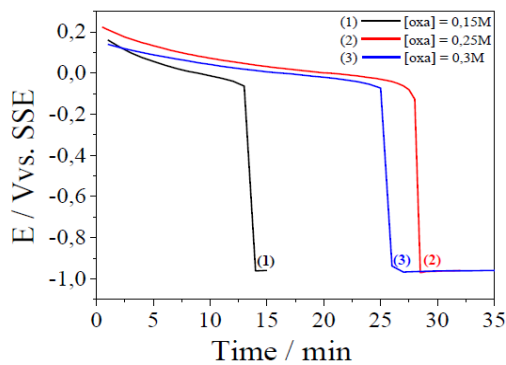

Figure 1. OCP curve versus time in H_2SO_4 pH 0.5 solution for PANI-coated steel polymerized at different oxalic acid concentrations. Synthesis time = 6 hours. i = 2 mA.cm^{-2}

The sudden drop in potential is used to estimate the time t_c at which the PANI coating loses its protective properties. However, after this drop, the PANI coating still provides some protection to the steel substrate through a simple polymer barrier effect. It is important to note that this effect is not taken into consideration when estimating the time of loss of protection [15].

According to figure 1, all the curves have the same starting with a positive potential but show different protection times.

The PANI layer synthesized in 0.25M oxalic acid shows a longer protection time, this result is linked to the quality of the film under these synthesis conditions, which provides galvanic anodic protection [8].

B.   Influence of synthesis time

Figure 2 shows the corrosion test results obtained on PANI films at different synthesis times.
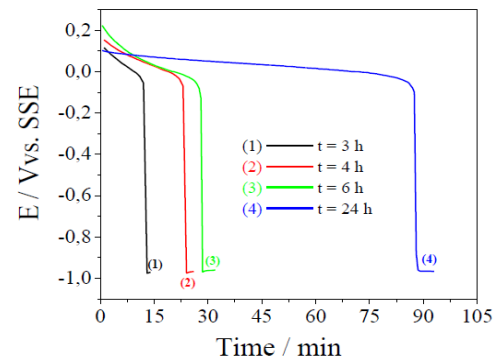

Figure 2. OCP curve versus time in H_2SO_4 pH 0.5 solution for PANI-coated steel polymerized in 0.25M oxalic acid at different synthesis times. i = 2 mA.cm^{-2}

It is noted that the protective effectiveness of the steel increases proportionally with the synthesis time of PANI films. This result is linked to the thickness of film formed and to quantity of electric charge available (see Table 1) that the film can deliver to ensure galvanic anodic protection. The thickness of the layer has considerable effects on the corrosion behavior of steel.

Table 1. Quantity of electricity consumed Qp for current density i = 2 mA.cm-2 at different synthesis times.

Synthesis time (h)	3	4	6	24
Q_p (mC.cm^{-2})	316	547	556	2122
Protection time (min)	12	24	28	88

The SEM analysis of the formed film at 6h of synthesis shows a uniform and homogeneous deposit, as shown in figure 3 (A). After 30 minutes immersion in H_2SO_4 pH0.3 (figure 3 (B)), we notice attacks depths of the coating translated by the development of lesions on the surface, leaving thus steel in its bare state.
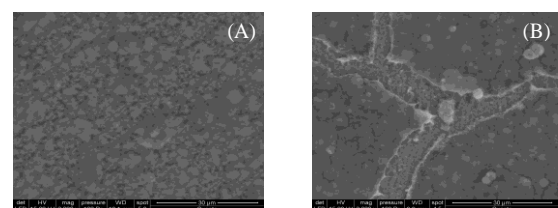

Figure 3. SEM picture of PANI-coated steel polymerized in 0.25M oxalic acid solution : (A) before and (B) after 30 min immersion in H_2SO_4 pH0.3

Biopolymer Applications Journal   <u>*Naima BRINIS et al. Vol 03. N°1, 2024, pp. 17-20*</u>

e-ISSN : 2800-1729

EIS studies

Electrochemical Impedance Spectroscopy (EIS) was used as a powerful complementary method to obtain additional information about the corrosion inhibition properties of PANI coatings. The impedance response represented on Nyquist diagram of PANI coating as a function of the immersion time in H_2SO_4 solution at 0.5 M is presented in figure 4. The synthesized time of the films is 6 hours.
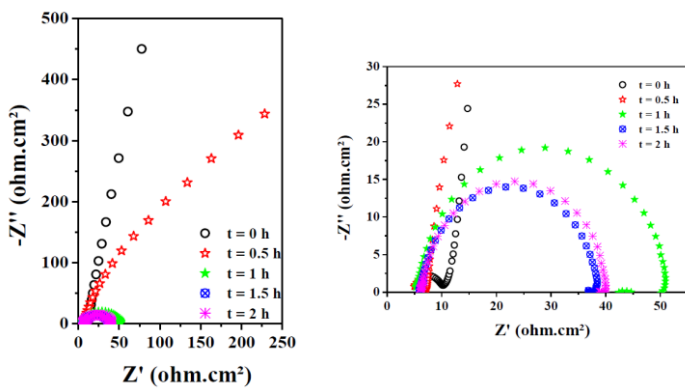
Figure 5. Evolution of the capacity and the free potential as a function of immersion time.

C. Influence of MoO_4^{-2} concentration

Results of corrosion tests carried out on PANI-MoO_4^{-2} films doped with molybdate ions at different concentrations are shown in figure 6. We see that the coatings doped with molybdate ions provide a clear improvement which is traducted by a significant increase of the protection time. This

behavior has already been observed in the works by Ohtsuka and al. [19] on films from polypyrrole. The presence of molybdate ions in coating seems to stabilize the passive film on surface of steel.

Figure 4. Impedance diagrams in H_2SO_4 pH0.3, at different immersion times of PANI coated. Synthesis time: 6 hours

It can be seen that the immersion time has a significant effect on the impedance of PANI coatings. Result of impedance plots obtained at a short immersion time shows a linear region which means that film behaves as a blocked electrode [8] exhibiting the characteristics of a corrosion reaction inhibited by mass transfer limitations [16]. PANI act as a barrier against the diffusion of the electrolyte (H_2SO_4) and aggressive ions (SO_4^{-2}), protecting the metal.

When the immersion time is longer, the linear region is transformed into a semicircle possibly having the characteristics of a diffusion impedance and attributed to various factors related to the corrosion behavior of the metal in the given environment. The size of the loop corresponds to the charge transfer resistance R_{ct}, and the increase in the values of the capacitance C_{dl} shown on the figure 5 may be due to acid attack on metal [17, 18].
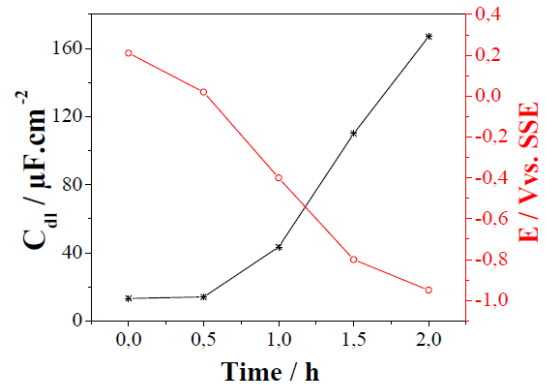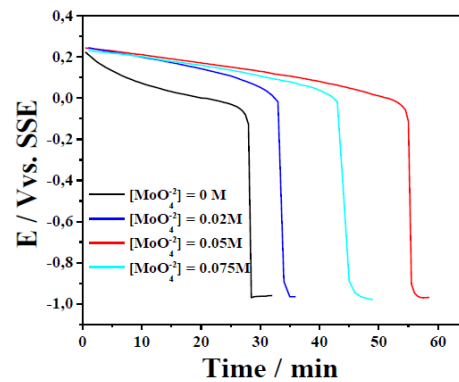
Figure 6. OCP curve versus time in H_2SO_4 pH 0.5 solution for PANI-coated steel doped with molybdate ions. Synthesis time = 6 h.

We have grouped in Table 2 the quantity of electricity applied and the protection time values to the different concentrations of molybdate studied. A better protection of the steel was obtained for an optimal concentration of 0.05 M.

Table 2. Quantity of electricity consumed Qp for current density i = 2 mA.cm-2 at different concentartions of MoO_4^{-2}.

Na_2MoO_4 concentration (M)	0	0.02	0.05	0.075
Q_p (mC.cm^{-2})	556	5231	1712	2894
Protection time (min)	28	34	55	45

IV. Conclusions

This study allowed us to identify the most appropriate experimental conditions for the synthesis of organic coatings based on polyaniline on a steel surface. The coatings are able to offer protection in the acidic medium H_2SO_4.

An improvement in the performance of these coatings has been proposed by doping anions in the structure of the films produced. This improvement could be the result of self-healing of the underlying passive layer. As a result, when the steel surface is attacked by corrosive agents, the conductive polymer is reduced resulting in the expulsion of counter anions. These once released can self-repair the film by the in-situ formation of a passive layer at the site of the lesions.

These findings suggest that doping polyaniline coatings holds promise for corrosion protection of steel, although further research is needed to fully understand the mechanisms and optimize the effectiveness of these coatings.

The use of conducting polymers in corrosion protection offers a promising avenue for addressing the challenges associated with metal corrosion, providing innovative solutions for preserving the integrity of metal surfaces.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported.

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